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THE OVERHAUSER EFFECT IN PARAMAGNETIC SYSTEMS

by

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INTRODUCTION

The first half of this report, in Sections 1-5 inclusive, is devoted to a discussion of the theory of the Overhauser nuclear polarization effect, and particular attention is paid to the expected sign of the nuclear magnetization. A negative nuclear polarization in which the higher nuclear Zeeman levels are more populated than the lower energy levels could be used as a low-noise quantum mechanical amplifier of radiofrequency signals. In the second half of the report, in Sections 6-11 inclusive, is considered various systems which have or might be investigated experimentally by simultaneous saturation of the electron or hole spin resonance and observation of an appropriate nuclear magnetic resonance frequency. There are several systems which should present very interesting results: Be^9 , donors in Ge, acceptors in Ge and Si, Ag^0Ag^+ in KCl, F_2^- in LiF.

This report does not review all the possible paramagnetic systems. For example, there is no discussion of paramagnetic resonance in crystals containing ions with an unfilled d or f shell. These systems are of current interest in connection with MASER work and there is a definite possibility that saturation of the electron spin resonance will result in an inversion of the nuclear population distribution, which could then be detected by induced emission of a nuclear resonance frequency. Such a case has recently been reported and involves the negative polarization of Al^{27} nuclei in ruby. This experiment can be understood in terms of the theory of dynamic polarization.

There are several important double resonance techniques which have not been considered in this report. These are dynamic polarization, ENDOR, and optical pumping. These are all sufficiently closely related to the Overhauser effect that a discussion of their relative merits would be most instructive.

This report makes reference to most of the theoretical papers on the Overhauser effect and to all of the available experimental papers. Some of the more important papers on other double resonance methods are listed below.

Dynamic Polarization

- A. Abragam and W. Proctor, *Comptes Rendus* 246, 2256 (1958).
- Uebersfeld, Motchane, and Erb, *J. Phys. Rad.* 19, 843 (1958).
- J. A. Cowen, W. A. Schafer, and R. D. Spence, *Phys. Rev. Letters* 3, 27 (July 1959)

ENDOR

J. H. Burgess and R. E. Norberg, Phys. Rev. 100, 752 (1955)
 G. Feher, Phys. Rev. 103, 834 (1956)

Optical Pumping

Brossel and Kastler, Phys. Rev. 79, 196, 225 (1950)
 Brossel and Bitter, Phys. Rev. 86, 309 (1952)

Paramagnetic Resonance in Transition Group Ion Impurities

B. Bleaney and K. W. H. Stevens, Rep. Prog. Phys. 16, 108 (1953)
 K. D. Bowers and J. Owen, Rep. Prog. Phys. 18, 304 (1955)
 D. M. S. Bagguley and J. Owen, Rep. Prog. Phys. 20, 304 (1957)

SECTION I

Nuclear Magnetization

Consider a system of $N(n)$ identical noninteracting nuclei. Each nucleus has a total angular momentum $\vec{I}\hbar$ and a magnetic moment $\vec{\mu}_n$ proportional to the angular momentum such that

$$\vec{\mu}_n = \gamma_n \hbar \vec{I} \quad , \quad (1.1)$$

where γ_n is the proportionality factor. In a constant external magnetic field, $\vec{H}_0$, each nuclear magnet has an orientational potential energy:

$$V_m = -\vec{\mu}_n \cdot \vec{H}_0 = -\gamma_n \hbar H_0 m_I \quad , \quad (1.2)$$

where $-I \leq m_I \leq I$. If E_0 denotes the energy of a nucleus in the absence of a magnetic field, the possible energy levels,

$$E_{m_I} = E_0 - \gamma_n \hbar H_0 m_I \quad (1.3)$$

of a nucleus in a magnetic field are represented in Fig. (1a) for $\gamma_n > 0$, $I = \frac{3}{2}$ and in Fig. (1b) for $\gamma_n < 0$, $I = \frac{1}{2}$. Equation (1.3) applies to nuclei whose gyromagnetic ratio, γ_n , is either positive or negative. As is indicated in Fig. 1, if $\gamma_n > 0$, the ground state has the largest positive value of m , and if $\gamma_n < 0$ the ground state has the largest negative value of m . In thermal equilibrium at temperature T the ratio of the population of nuclei in different Zeeman levels m , m' is given by the Boltzmann factor

$$\frac{N(m)}{N(m')} = \exp \frac{(E_{m'} - E_m)}{kT} = \exp \frac{\gamma_n \hbar H_0 (m - m')}{kT} \quad . \quad (1.4)$$

Fig. 1a

$$\gamma_n > 0, I = \frac{3}{2}$$

Fig. 1b

$$\gamma_n < 0, I = \frac{1}{2}$$

Thus

$$\frac{N(3/2)}{N(1/2)} = \exp \frac{\gamma_n \hbar H_0}{kT} = \exp \frac{|\gamma_n| \hbar H_0}{kT}, \gamma > 0 \quad (1.4a)$$

and

$$\frac{N(-1/2)}{N(1/2)} = \exp \left(\frac{-\gamma_n \hbar H_0}{kT} \right) = \exp \frac{|\gamma_n| \hbar H_0}{kT}, \gamma < 0 \quad (1.4b)$$

It is clear that Eq. (1.4) automatically takes into account negative as well as positive γ_n 's, so that the most populated state is always the ground state. The total magnetization $M_0^{(n)}$ in the direction of H_0 is simply

$$M_0^{(n)} = \gamma_n \hbar \sum_{-I}^I N(m_I) m_I, \quad (1.5)$$

which, by the use of Eqs. (1.3) and (1.4), may be written

$$M_0^{(n)} = N^{(n)} \gamma_n \hbar \left\{ \frac{2I+1}{2} \operatorname{ctnh} \left[\frac{(2I+1)\alpha}{2} \right] - \frac{1}{2} \operatorname{ctnh} \left(\frac{\alpha}{2} \right) \right\}, \quad (1.6)$$

where

$$N^{(n)} = \sum_{-I}^I N(m_I)$$

is the total number of nuclei and

$$\alpha = \gamma_n \hbar H_0 / kT \quad . \quad (1.7)$$

This nuclear magnetization is always positive irrespective of the sign of γ . For small values of α we use the expansion

$$\text{ctnh}x \approx \frac{1}{x} + \frac{x}{3}$$

to obtain the approximate value:

$$M_0^{(n)} = N^{(n)} \gamma_n \hbar \left\{ \frac{1}{3} I(I+1) \alpha \right\} = \frac{N^{(n)} \gamma_n^2 \hbar^2 H_0}{3kT} I(I+1) \quad . \quad (1.8)$$

The nuclear polarization, P_0 , and susceptibility, χ_0 are related to M_0 by the following definitions:

$$P_0^{(n)} \equiv M_0^{(n)} / N^{(n)} \hbar \gamma_n \approx \gamma_n \hbar H_0 (I+1) / 3kT \quad (1.9)$$

for $\gamma_n \hbar H_0 \ll kT$

$$\chi_0^{(n)} \equiv M_0^{(n)} / H_0 \approx N^{(n)} \gamma_n^2 \hbar^2 I(I+1) / 3kT \quad . \quad (1.10)$$

In this section material has been presented, in a somewhat amplified form, of a very well known subject as found, for example, in Pake's review of nuclear magnetic resonance.⁽¹⁾

SECTION 2

Electronic Magnetization

In principle electron paramagnetic resonance may take place in a system in which there is an electron whose spin is unpaired. There are a number of such systems which we will treat in detail in subsequent sections of this report.

Consider a system of $N^{(e)}$ electrons, each with spin $\vec{s}\hbar$ and magnetic moment $\vec{\mu}_e = \gamma_e \vec{s}\hbar$. In a constant magnetic field $\vec{H}_0$ each electronic magnet has an orientational potential energy

$$V_{m_s} = -\vec{\mu}_e \cdot \vec{H}_0 = -\gamma_e \hbar H_0 m_s \quad , \quad (2.1)$$

where $m_s = \pm \frac{1}{2}$. In Fig. 2 the electron Zeeman levels are indicated. Note that, since $\gamma_e < 0$, the $m_s = -\frac{1}{2}$ state is the ground state, corresponding to an electronic magnet oriented parallel to $\vec{H}_0$. Let $N_0(-)$ denote the equilibrium number of electrons with spin parallel (magnetic moment anti-parallel) to the magnetic field and $N_0(+)$ the equilibrium number of oppositely oriented electrons:

$$N_0(-) + N_0(+) = N^{(e)} \quad . \quad (2.2)$$

The explicit form for the equilibrium magnetization,

$$M_0^{(e)} \equiv \frac{1}{2} \hbar |\gamma_e| [N_0(-) - N_0(+)] \quad , \quad (2.3)$$

depends upon whether the electrons are treated as a degenerate Fermi gas, as in a metal, or classically, using Boltzmann statistics, as in a non-conducting paramagnetic.

Fig. 2

Suppose now that we place the system in a magnetic field which has a static and a time-dependent component at right angles to one another:

$$\vec{H} = H_0 \vec{k} + 2H_1 \cos \omega t \vec{i} \quad . \quad (2.4)$$

Bloch's⁽²⁾ well-known phenomenological formulation of this problem for nuclear magnetic resonance is equally applicable for the case of electron paramagnetic resonance:

$$\frac{d\vec{M}^{(e)}}{dt} - \gamma_e (\vec{M}^{(e)} \times \vec{H}) + \frac{M_x^{(e)}}{T_2^{(e)}} \vec{i} + \frac{M_y^{(e)}}{T_2^{(e)}} \vec{j} + \frac{M_z^{(e)} - M_0^{(e)}}{T_1} \vec{k} = 0 \quad . \quad (2.5)$$

The steady-state (slow passage) solution of the differential Eq. (2.5) for the components of the electronic magnetization $M^{(e)}$ is

$$\left. \begin{aligned} M_x^{(e)} &= \frac{1}{2} \chi_0^{(e)} \omega_0 T_2^{(e)} \left[\frac{2H_1 \cos \omega t (\omega_0 - \omega) T_2^{(e)} + 2H_1 \sin \omega t}{1 + (\omega_0 - \omega)^2 T_2^{(e)^2} + \gamma_e^2 H_1^2 T_1^{(e)} T_2^{(e)}} \right] \\ M_y^{(e)} &= \frac{1}{2} \chi_0^{(e)} \omega_0 T_2^{(e)} \left[\frac{2H_1 \cos \omega t - 2H_1 \sin \omega t (\omega_0 - \omega) T_2^{(e)}}{1 + (\omega_0 - \omega)^2 T_2^{(e)^2} + \gamma_e^2 H_1^2 T_1^{(e)} T_2^{(e)}} \right] \\ M_z^{(e)} &= \chi_0^{(e)} H_0 \left[\frac{1 + (\omega_0 - \omega)^2 T_2^{(e)^2}}{1 + (\omega_0 - \omega)^2 T_2^{(e)^2} + \gamma_e^2 H_1^2 T_1^{(e)} T_2^{(e)}} \right] \end{aligned} \right\} \quad (2.6)$$

where $\chi_0^{(e)} = M_0^{(e)}/H_0$, $\omega_0 = |\gamma_e| H_0$, and $T_1^{(e)}$ and $T_2^{(e)}$ are the electron spin lattice and electron spin-spin relaxation times, respectively.

It is clear that a sufficiently large value of H_1 will reduce $M_z^{(e)}$ to zero. There are several "saturation parameters" used in the literature, which are defined as follows:

$$\left. \begin{aligned} s_1 &\equiv 1 - \frac{M_z^{(e)}}{M_0^{(e)}} \quad 0 \leq s_1 \leq 1 \\ s_2 &\equiv \gamma_e^2 H_1^2 T_1^{(e)} T_2^{(e)} \\ s_3 &\equiv \left[1 + \gamma_e^2 H_1^2 T_1^{(e)} T_2^{(e)} \right]^{-1} = [1 + s_2]^{-1} \end{aligned} \right\} \quad (2.7)$$

The saturation parameter used in discussions of the Overhauser nuclear polarization effect is s_1 , which we will henceforth denote by s .

It is possible to obtain relatively simple expressions for H_1 and for the power W absorbed by the substance in terms of s , $\chi_0^{(e)}$, $T_1^{(e)}$, $T_2^{(e)}$ and the static field H_0 . From Eqs. (2.6) and (2.7),

$$H_1 = \frac{1}{|\gamma_e| \sqrt{T_1^{(e)} T_2^{(e)}}} \left\{ \frac{s [1 + (\omega_0 - \omega)^2 T_2^{(e)^2}]}{1 - s} \right\}^{1/2} \quad (2.8)$$

and

$$W = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} H_x \frac{dM_x^{(e)}}{dt} dt = \frac{s \omega M_0^{(e)}}{|\gamma_e| T_1^{(e)}} = \frac{s \omega \chi_0^{(e)} H_0}{|\gamma_e| T_1^{(e)}} \quad (2.9)$$

At resonance, $\omega = \omega_0 = |\gamma_e|H_0$, and these expressions reduce to

$$H_1 = \frac{1}{|\gamma_e| \sqrt{T_1^{(e)} T_2^{(e)}}} \left[\frac{s}{1-s} \right]^{\frac{1}{2}} \quad (2.8a)$$

and

$$W = s \chi_0^{(e)} H_0^2 / T_1^{(e)}, \quad (2.9a)$$

as shown by Brovetto and Cini.⁽³⁾ The simple result expressed by Eq. (2.9) may seem somewhat strange at first sight because it says that a paramagnetic substance will absorb more energy per unit time for values of ω greater than the resonant frequency ω_0 . However, this is for a constant value of saturation s , which is related to $\vec{\omega}$ through Eq. (2.8) as follows:

$$s = \frac{H_1^2 \gamma_e^2 T_1^{(e)} T_2^{(e)}}{1 + (\omega_0 - \omega)^2 T_2^2 + H_1^2 \gamma_e^2 T_1^{(e)} T_2^{(e)}} \quad (2.10)$$

attains its maximum value at resonance.

SECTION 3

Nuclear Polarization by the Overhauser Effect

Suppose now that our $N^{(n)}$ nuclear spins and $N^{(e)}$ electron spins are placed simultaneously in a magnetic field $\vec{H} = H_0 \vec{k} + 2H_1 \cos \omega t \vec{i}$ and that they interact with one another via the contact part of the hyperfine interaction

$$\mathcal{H} = (8\pi/3) \gamma_e \gamma_n \hbar^2 \vec{I} \cdot \vec{S} \delta(\vec{r}) \quad (3.1)$$

$\vec{r}$ is illustrated in Fig. 3. Let us consider the limiting case of complete saturation of the electron spin resonance, i.e., $s = 1$. The energy levels of the electron spin and the nuclear spin are given to a good approximation by

$$E(m_S, m_I) = -\gamma_e \hbar H_0 m_S - \gamma_n \hbar H_0 m_I + a m_S m_I, \quad (3.2)$$

providing $|\gamma_e| \hbar H_0 \gg a$. In Fig. 4 the energy levels are sketched (not to scale) for $I = \frac{1}{2}$, $\gamma_n > 0$ and $\gamma_n < 0$. In this sketch we also neglect a in comparison with $|\gamma_n| \hbar H_0$. Figures (4a) and (4b) differ in one important respect. Since $\gamma_n < 0$ in (4b), the states with $m_I = -\frac{1}{2}$ are lower in energy than the states with $m_I = \frac{1}{2}$. In thermal equilibrium at temperature T

Fig. 3

Fig. 4a

$$\gamma_n > 0$$

Fig. 4b

$$\gamma_n < 0$$

$$\frac{N_1}{N_2} = \frac{N_3}{N_4} = \exp \frac{|\gamma_n| \hbar H_0}{kT} \quad (3.3)$$

and

$$\frac{N_1}{N_3} = \frac{N_2}{N_4} = \exp \frac{|\gamma_e| \hbar H_0}{kT} \quad (3.4)$$

Now suppose that the transitions $1 \leftrightarrow 3$ and $2 \leftrightarrow 4$ are simultaneously saturated so that

$$N_1/N_3 = N_2/N_4 = 1 \quad (3.5)$$

i.e., $s = 1$. The off-diagonal elements of $\mathcal{H}$, given in Eq. (3.1), induce relaxation processes in which the total spin angular momentum is conserved, i.e.,

$$\Delta m_S + \Delta m_I = 0 \quad . \quad (3.6)$$

These are transitions of the type $1 \leftrightarrow 4$ for $\gamma_n > 0$ (Fig. 4a) and of type $2 \leftrightarrow 3$ for $\gamma_n < 0$ (Fig. 4b). In the steady-state these levels will have a population ratio given by the appropriate Boltzmann factor:

$$\frac{N_1}{N_4} = \exp \frac{(|\gamma_e| + |\gamma_n|)\hbar H_0}{kT} \quad \text{for } \gamma_n > 0$$

and

$$\frac{N_2}{N_3} = \exp \frac{(|\gamma_e| - |\gamma_n|)\hbar H_0}{kT} \quad \text{for } \gamma_n < 0 \quad . \quad (3.7)$$

The ratio of nuclei with spin up to those with spin down is

$$\frac{N(+)}{N(-)} = \frac{N_1 + N_3}{N_2 + N_4} \quad \text{for } \gamma_n > 0 \quad (3.8)$$

and

$$\frac{N(+)}{N(-)} = \frac{N_2 + N_4}{N_1 + N_3} \quad \text{for } \gamma_n < 0 \quad . \quad (3.9)$$

Using Eqs. (3.5) and (3.7),

$$\frac{N(+)}{N(-)} = \frac{2N_1}{2N_4} = \exp \frac{(|\gamma_e| + |\gamma_n|)\hbar H_0}{kT} \quad \text{for } \gamma_n > 0 \quad (3.10)$$

and

$$\frac{N(+)}{N(-)} = \frac{2N_2}{2N_3} = \exp \frac{(|\gamma_e| - |\gamma_n|)\hbar H_0}{kT} \quad \text{for } \gamma_n < 0 \quad . \quad (3.11)$$

The steady-state nuclear magnetization, $M^{(n)}$, is given by an equation of exactly the same form as Eq. (1.6), but with a vastly different value for α .

$$M^{(n)} = N^{(n)} \gamma_n \hbar \left\{ \frac{2I + 1}{2} \operatorname{ctnh} \left(\frac{2I + 1}{2} \alpha \right) - \frac{1}{2} \operatorname{ctnh} \left(\frac{\alpha}{2} \right) \right\}, \quad (3.12)$$

where

$$\alpha = (|\gamma_e| + \gamma_n)\hbar H_0 / kT > 0 \quad . \quad (3.13)$$

Thus the sign of the Overhauser nuclear magnetization depends entirely on the sign of γ_n . The nuclear polarization may be defined either as

$$P \equiv M^{(n)}/N^{(n)} \hbar |\gamma_n|$$

or

$$P \equiv M^{(n)}/N^{(n)} \hbar \gamma_n .$$

The latter definition guarantees a positive nuclear polarization irrespective of the sign of M . We shall use the former definition so that P and M always have the same sign. Suppose the system is now subjected to a second time-varying magnetic field of frequency ω_2 close to $\omega_n = |\gamma_n|H_0$ such that the total external magnetic field is given by

$$\vec{H} = H_0 \vec{k} + 2H_1 \cos \omega_1 t \vec{i} + 2H_2 \cos \omega_2 t \vec{i} . \quad (3.14)$$

Let us call ω_1 the pumping or saturating frequency and ω_2 the detecting frequency. The power absorbed by the system will now be given to a good approximation by the sum of two terms:

$$W = \frac{s\omega_1 M_0^{(e)}}{|\gamma_e| T_1^{(e)}} + M^{(n)} \frac{H_2^2 \omega_2 |\gamma_n| T_2^{(n)}}{1 + T_2^{(n)} (\omega_n - \omega_2)^2 + \gamma_n^2 H_2^2 T_1^{(n)} T_2^{(n)}} . \quad (3.15)$$

The first term in Eq. (3.15) represents "pumping power" absorbed and was derived previously in Eq. (2.9). The second term represents rf power absorbed or emitted depending on the sign of $M^{(n)}$. The essential assumption in Eq. (3.15) is that the static nuclear magnetization, M_0 [Eq. (1.6)], which appears in the usual expression for power absorbed in nuclear magnetic resonance, be replaced by the steady-state Overhauser nuclear magnetization, $M^{(n)}$ [Eq. (3.12)]. For $\omega_1 = |\gamma_e|H_0$, $s \approx 1$, $\omega_2 = |\gamma_n|H_0$, and $\gamma_n^2 H_2^2 T_1^{(n)} T_2^{(n)} \ll 1$, Eq. (3.15) reduces to the simple form

$$W = \chi_0^{(e)} H_0^2 / T_1^{(e)} + \chi^{(n)} H_2^2 \omega_n^2 T_2^{(n)} , \quad (3.16)$$

where $\chi^{(n)}$ is the steady-state nuclear susceptibility. For $I = \frac{1}{2}$ and $\alpha \ll 1$,

$$\chi^{(n)} \approx N^{(n)} \gamma_n |\gamma_e| \hbar^2 / 4kT . \quad (3.17)$$

With these approximations the ratio of the power absorbed by the nuclear spin system to the power absorbed by the saturated electron spin system is

$$W^{(n)}/W^{(e)} = N^{(n)} \gamma_n^3 |\gamma_e| \hbar^2 H_2^2 T_1^{(e)} T_2^{(n)} / 4kT \chi_0^{(e)} . \quad (3.18)$$

The discussion presented in Section 3 of this report represents a simple extension of Pake's derivation⁽¹⁾ of the Overhauser effect to the case of negative nuclear magnetic moments. It clearly shows that an inverted nuclear population distribution may be obtained by saturating the electron spin resonance providing three conditions are satisfied:

- (1) $\gamma_e < 0$;
- (2) $\gamma_n < 0$;
- (3) $\Delta m_S + \Delta m_I = 0$.

Condition (1) is satisfied if the "unpaired electron" is a single electron outside a closed subshell. Condition (2) is satisfied by a considerable number of nuclei whose magnetic moments are negative. Condition (3) is satisfied if $\vec{I} \cdot \vec{S}$ coupling dominates over ordinary dipolar coupling. We will examine these conditions in more detail in subsequent sections of this report, and we will find that other sets of conditions also give rise to negative nuclear magnetization. An inverted nuclear population distribution of this type is of interest because of the possibility of using such a system as a low noise rf amplifier.

SECTION 4

A Thermodynamic Treatment of the Overhauser Effect

It is interesting to examine a second derivation of the Overhauser effect by means of a simple thermodynamic argument due to Brovetto and Cini.⁽⁴⁾ Consider again electrons and nuclei coupled by the contact part of the hyperfine interaction, which we shall write now in terms of the familiar raising and lowering operators:

$$\mathcal{H} = (8\pi/3) \gamma_e \gamma_n \hbar^2 (I_z S_z + 2I_+ S_- + 2I_- S_+) \delta(\vec{r}) \quad , \quad (4.1)$$

where

$$I_{\pm} = (I_x \pm iI_y)/2$$

and

$$S_{\pm} = (S_x \pm iS_y)/2 \quad .$$

The second and third terms in the parenthesis of Eq. (4.1) induce simultaneous nuclear and electronic spin flips of the type

$$e_{\frac{1}{2}} + n_{-\frac{1}{2}} \longleftrightarrow e_{-\frac{1}{2}} + n_{\frac{1}{2}} \quad , \quad (4.2)$$

where $e_{\pm 1/2}$ denotes an electron with spin parallel (+) and antiparallel (-) to the magnetic fields; $n_{\pm 1/2}$ has a similar meaning for nuclear spins. For simplicity we choose $I = \frac{1}{2}$. The results, as in Section 3, may be readily extended to any value of I . The important point to note here is that the subscript on e and n denotes the spin orientation, not the orientation of the corresponding magnetic moment. The term I_+S_- flips a nuclear spin from down to up and an electron spin from up to down. The transitions induced by this operator are those which proceed from left to right in Eq. (4.2). The term I_-S_+ induces transitions from right to left in Eq. (4.2). Let $N(+)$ be the number of $n_{1/2}$, and $N(-)$ be the number of $n_{-1/2}$; let $N(\frac{1}{2})$ be the number of $e_{1/2}$ and $N(-\frac{1}{2})$ be the number of $e_{-1/2}$. When the transitions represented by Eq. (4.2) come to an equilibrium or steady-state the law of mass action provides us with a relationship between the occupation numbers of the "chemical" constituents:

$$\frac{N(-\frac{1}{2})}{N(+\frac{1}{2})} \frac{N(+)}{N(-)} = K \quad , \quad (4.3)$$

where K may be obtained by integrating the Van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta U}{RT^2} \quad , \quad (4.4)$$

where R is the gas constant. We must be careful about the evaluation of ΔU . The transitions represented by Eq. (4.1) do not conserve energy. The dominant transition is the one in which energy is taken out of the spin system and transferred to the lattice and not vice versa. This is the transition induced by the operator I_+S_- . The change in internal energy of the spin system during this process is

$$\Delta U = -N(|\gamma_e| + \gamma_n)\hbar H_0 \text{ for } \gamma_n > 0 \quad (4.5)$$

and

$$\Delta U = -N(|\gamma_e| - |\gamma_n|)\hbar H_0 \text{ for } \gamma_n < 0 \quad ,$$

where N is taken as Avogadro's number. This result may be easily obtained with the aid of Fig. 5.

$$\ln K = \ln \left[\frac{N(-\frac{1}{2})N(+)}{N(+\frac{1}{2})N(-)} \right] = - \frac{\Delta U}{RT} + \text{const.} = \frac{(|\gamma_e| + \gamma_n)\hbar H_0}{kT} + \text{const.} \quad (4.6)$$

at $T = \infty$, $N(-\frac{1}{2}) = N(+\frac{1}{2})$ and $N(+)=N(-)$, which means that the const. is equal to 0. Therefore,

$$\frac{N(-\frac{1}{2})}{N(+\frac{1}{2})} \frac{N(+)}{N(-)} = \exp \frac{(|\gamma_e| + \gamma_n)\hbar H_0}{kT} \quad (4.7)$$

Electron Spin Zeeman Levels

Fig. 5

Nuclear Spin Zeeman Levels

If the electron spin system is saturated by intense microwaves of frequency $\omega = |\gamma_e|H_0$, the transitions $e_{-\frac{1}{2}} + \hbar\omega \rightarrow e_{+\frac{1}{2}}$ increase the $N(+\frac{1}{2})$ population, and the relaxation process $e_{+\frac{1}{2}} + n_{-\frac{1}{2}} \rightarrow e_{-\frac{1}{2}} + n_{+\frac{1}{2}}$ will induce nuclear polarization. In the limit for $s = 1$, when $N(+\frac{1}{2}) = N(-\frac{1}{2})$, we have, from Eq. (4.7),

$$\frac{N(+)}{N(-)} = \exp \frac{(|\gamma_e| + \gamma_n)\hbar H_0}{kT} \quad (4.8)$$

in agreement with Eq. (3.7). This result holds for either sign of γ_n . From Fig. 5 it is clear that the upper nuclear Zeeman level is more populated than the lower when γ_n is negative.

SECTION 5

Results of Generalized Treatments of the Overhauser Effect

There are two papers^(5,6) which give a more general and rigorous treatment of the Overhauser effect, where results are of importance both for the interpretation of experiments which have been performed and for the suggestion of experiments which might be worthwhile doing.

In the paper by Barker and Mencher⁽⁵⁾ it is shown that the thermodynamic argument of Brovetto and Cini,⁽⁴⁾ which is summarized in Section 4, can be justified on the basis of the thermodynamics of irreversible

processes. The Overhauser effect is found to be a steady state of minimum production of entropy. Formulae are derived which apply to relaxation processes other than that due to the contact part of the hyperfine interaction. The nuclear magnetization, $M^{(n)}$, has exactly the same form as in Eqs. (1.6) and (3.12), but the argument α of the Brillouin function is found to be more complex.

In a metal where the conduction electrons must be described using Fermi-Dirac statistics,

$$\alpha_{FD} = [\gamma_n + s|\gamma_e|(f^{(1)} - f^{(2)})] \hbar H_0 / kT \quad , \quad (5.1)$$

where $f^{(i)}$ denotes the fraction of nuclei having spin reversed which relax by process i with $i = 1, 2, 3$. Process 1 we have already discussed; it is that process described by the reaction equation

in which $\Delta m_I + \Delta m_S = 0$. Here n_m denotes a nucleus with component m of the spin angular momentum I in the direction of the external magnetic field H_0 . Process 2 is described by the reaction equation

in which $\Delta m_S + \Delta m_I = \pm 2$. Process 3 is described by the reaction equation

in which a nuclear spin is flipped without an accompanying electron spin flip. The contact part of the hyperfine interaction induces nuclear relaxation by process 1, in which nuclear plus electron spin angular momentum is conserved. The dipolar part of the hyperfine interaction induces nuclear relaxation by processes (1), (2) and (3). There are of course other interactions which induce nuclear relaxations of process 3. We note that the nuclear spin lattice relaxation times are related to the $f^{(i)}$'s as follows:

$$f^{(i)} = T_1^{(n)} / T_1^{(n)(i)} \quad (5.5)$$

where $T_1^{(n)}$ is the total nuclear spin lattice time and $T_1^{(n)(i)}$ the nuclear spin lattice relaxation time associated with process i . If we assume that processes (1), (2) and (3) represent all possible nuclear spin lattice relaxation mechanisms it is clear that

$$\sum_{i=1}^3 f^{(i)} = 1 \quad . \quad (5.6)$$

It should be noted that $f^{(3)}$ is included implicitly in Eq. (5.1) through Eq. (5.6) and may considerably reduce the nuclear polarization.

In a nonmetal where the unpaired electron spins do not form a degenerate Fermi gas, one may use Boltzmann statistics for the electrons, with the result that α is given by

$$\alpha_B = \frac{[\gamma_n + (f^{(1)} - f^{(2)}) |\gamma_e|] \hbar H_0}{kT} - 2(f^{(1)} - f^{(2)}) \tanh^{-1} \left[(1-s) \tanh \frac{(|\gamma_e| \hbar H_0)}{2kT} \right] \quad (5.7)$$

Note that in the limiting case of complete saturation of the electron spin resonance ($s=1$), α_{FD} and α_B are identical and are given by Eq. (3.13). In the absence of a time-varying field we set $s = 0$ in Eqs. (5.11) and (5.7) and recover the equilibrium expression for α , given in Eq. (1.7). For intermediate values of the saturation parameter between 0 and 1, $\alpha_B > \alpha_{FD}$. This means that one can obtain a higher nuclear polarization for a given $s < 1$ in a nonmetal than in a metal. This important practical point was made by Brovetto and Ferroni.⁽⁷⁾

There is a serious question as to whether or not the expression for the steady-state nuclear magnetization as given by Eqs. (3.12), (5.1) and (5.7) is valid at low temperatures. At the present time this point has not yet been investigated experimentally. From the theoretical point of view there is an important restriction discussed both by M. Klein⁽⁸⁾ and by Barker and Mencher.⁽⁵⁾ These investigators find essentially that the condition

$$|\gamma_e| \hbar H_0 \ll kT \quad (5.8)$$

must be satisfied in order to obtain the quoted results using thermodynamic arguments. The restriction is somewhat less severe in the paper by Barker and Mencher.⁽⁵⁾ Recent calculations on the nuclear spin specific heat associated with Overhauser polarization indicates strongly that one must take these validity requirements seriously and that the expressions for the Overhauser effect when $|\gamma_e| \hbar H_0$ is comparable to kT are not known theoretically (at least using thermodynamic arguments). These specific heat calculations have been made by Barker, Desloge, and Neusel and have so far been reported only at meetings of the American Physical Society. A more thorough discussion of this important point will be published in the Physical Review in the near future.

Detailed kinetic calculations using an explicit Hamiltonian and perturbation theory have been made on the Overhauser effect by Overhauser,⁽⁹⁾ Abragam,⁽¹⁰⁾ and by Barker and Mencher.⁽⁵⁾

We shall review here Abragam's results for four cases of nuclear magnetic resonance:

- I. in a liquid containing paramagnetic impurities;
- II. in a metal;
- III. in a diamagnetic containing paramagnetic impurities; and
- IV. in a paramagnetic ion.

In each case we shall consider the electron spin resonance to be completely saturated. The question is to what extent, if any, does the nuclear spin system acquire an enhanced positive or negative magnetization. The basic Hamiltonian is of the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'(t) \quad (5.9)$$

where the static Hamiltonian

$$\mathcal{H}_0 = \gamma_e \hbar S_z H_0 - \gamma_n \hbar I_z H_0 + \vec{I} \cdot \vec{A}_0 \cdot \vec{S} \quad (5.10)$$

determines the energy levels of the system and the time-varying perturbing Hamiltonian

$$\mathcal{H}'(t) = \vec{I} \cdot \vec{A}_1 \cdot \vec{S} + \gamma_e \hbar \vec{H}' \cdot \vec{S}$$

induces transitions between different eigenstates of $\mathcal{H}_0$. Now $\vec{A} = \vec{A}_0 + \vec{A}_1(t)$ is a symmetrical tensor with a static and a time-varying component which provides a convenient shorthand for writing the magnetic interaction between an electron spin $\vec{S}$ and a nuclear spin $\vec{I}$. Also $\vec{H}'$ represents the fluctuating magnetic field produced by the lattice and is responsible for producing relaxation of electron spins.

Case 1: Nuclear Resonance in a Liquid Containing Paramagnetic Impurities

The principal assumptions made here are that (a) the electron-nuclear spin interaction is the classical dipole-dipole interaction, (b) the static part of the electron-nuclear dipole-dipole interaction averages to zero, and (c) the nuclear relaxation is provided by the relative motion of the paramagnetic ion and the nucleus. The energy level scheme of an electron plus a nucleus in a liquid is given in Fig. 5. Abragam uses the notation 2Δ = electron energy splitting $\approx |\gamma_e| \hbar H_0 / kT$ and 2δ = nuclear energy splitting/ kT . In this case $2\delta \approx \gamma_n \hbar H_0 / kT$ and the algebraic sign of δ is the same as that of γ_n . The explicit assumption is made that Δ and δ are small compared to unity. The classical dipole-dipole interaction,

$$\mathcal{H}_{\text{dipole-dipole}} = -\gamma_n \gamma_e \hbar^2 \left[\frac{\vec{I} \cdot \vec{S}}{r^3} - \frac{3(\vec{I} \cdot \vec{r})(\vec{S} \cdot \vec{r})}{r^5} \right] , \quad (5.11)$$

contains relaxation mechanisms of type (1), (2) and (3) [Eqs. (5.2), (5.3) and (5.4)]. This may be seen explicitly by writing Eq. (5.11) in terms of spherical polar coordinates as is done in reference 10 and in the well known BPP paper.⁽¹¹⁾ It is assumed that the spectral intensities of the interactions are frequency independent or "white" for all transitions involved and that the problem is isotropic, so that one can average the squares of the matrix elements over the angles. It is found⁽¹²⁾ that $f^{(1)}$; $f^{(2)}$; $f^{(3)} = 2:12:6$, so that

$$\frac{N_+}{N_-} \cong 1 - \Delta = 1 - \frac{1}{2} \frac{|\gamma_e| \hbar H_0}{kT} \quad (5.11a)$$

in the limit of complete saturation of the electron spin resonance. To interpret this result we must refer again to Fig. 5. For $\gamma_n > 0$, Eq. (5.10) gives a negative nuclear polarization; for $\gamma_n < 0$, Eq. (5.10) gives a positive nuclear polarization.

Case II. Nuclear Resonance in a Metal

The important electron spin-nuclear spin interaction in a metal is the contact part of the hyperfine interaction:

$$\mathcal{H}_{\text{contact}} = (8\pi/3) \gamma_e \gamma_n \hbar^2 \vec{I} \cdot \vec{S} \delta(\vec{r}) , \quad (5.12)$$

whose static part is responsible for the Knight shift and whose time-varying part produced by the relative motion of the nuclei and the conduction electrons induces relaxations in which $f^{(1)} \approx 1$ and

$$\frac{N_+}{N_-} \cong 1 + 2\Delta = 1 + \frac{|\gamma_e| \hbar H_0}{kT} \quad (5.13)$$

when the electron spin resonance is saturated. For $\gamma_n > 0$, Eq. (5.13) gives a positive nuclear polarization; for $\gamma_n < 0$, Eq. (5.13) gives a negative nuclear polarization

Case III: Nuclear Resonance in a Diamagnetic Crystal Containing Paramagnetic Impurities

No Overhauser effect is to be expected under the following assumptions:

(1) The relaxation of the nuclear spins is produced by the random flips of the electron spins rather than through their relative motion.⁽¹³⁾

(2) The dipole-dipole interaction is much smaller than the nuclear splitting $2\delta kT$. Otherwise no NMR would be observed.

(3) The electron-nuclear interaction is dipole-dipole rather than $\vec{I} \cdot \vec{S}$. An Overhauser effect would be observed if the interaction were $\vec{I} \cdot \vec{S}$, but this would increase the nuclear relaxation time by a factor of 10^6 -- an unrealistic result.

As a consequence of these assumptions, $f^{(3)} \approx 1$ and therefore

$$N_+/N_- \cong 1 + 2\delta \quad . \quad (5.14)$$

Case IV: Overhauser Effect in a Paramagnetic Ion

In this example the nucleus under consideration is in a paramagnetic ion. It is assumed that the hyperfine structure is resolved, which means that the tensor A_0 is diagonal and reduces to a single constant A_0 . The Hamiltonian for the electron-nuclear system is

$$\begin{aligned} \mathcal{H} = & \gamma_e \hbar H_0 S_z + A_0 S_z I_z + \frac{1}{2} A_0 (S_+ I_- + S_- I_+) - \gamma_n \hbar H_0 I_z \\ & + \vec{I} \cdot \vec{A}_1 \cdot \vec{S} + \gamma_e \hbar \vec{H}' \cdot \vec{S} \quad . \end{aligned} \quad (5.15)$$

Unlike the cases previously treated, the local magnetic field due to the electron in the ion is much larger than the external magnetic field at the nucleus. Thus we neglect the fourth term in comparison with the second and third. We also consider the strong-field or Paschen-Bach case. Hence,

$$|\gamma_e| \hbar H_0 \gg |A_0| \gg |\gamma_n| \hbar H_0 \quad . \quad (5.16)$$

Now A_0 has the same algebraic sign as γ_n . The energy-level diagram and eigenstates are given in Fig. 6a for $\gamma_n > 0$ and in Fig. 6b for $\gamma_n < 0$. In this diagram

$$\left. \begin{aligned} 2\Delta &= \frac{|\gamma_e| \hbar H_0}{kT} \quad , \quad p^2 + q^2 = 1 \quad , \\ 2\delta &= \frac{A_0}{2kT} \quad , \quad q \approx \frac{2A_0}{|\gamma_e| \hbar H_0} \quad , \quad p \approx 1 \end{aligned} \right\} \quad (5.17)$$

The first algebraic sign in the eigenstates (a'), (b'), etc., refers to S_z , the second to I_z .

The eigenstates (a) and (a') are essentially nuclear spin up states while (b) and (b') are essentially nuclear spin down states. The magnetic moment of the electron produces a large magnetic field at the nucleus. Consequently the nuclear magnet orients itself with respect to this field rather than with respect to the external field. Thus for electron spin down (up) a nucleus with positive gyromagnetic ratio has nuclear spin up (down) in the lower energy state. This situation is reversed for a nucleus with a negative gyromagnetic ratio.

Fig. 6a
 $\gamma_n > 0$

Fig. 6b
 $\gamma_n < 0$

Let us assume that both electron resonances are saturated, i.e., $a = a'$, $b = b'$, where a , a' , b , and b' denote the populations of the corresponding states (a) , (a') , etc. The term $\vec{I} \cdot A_1 \cdot \vec{S}$ produces nuclear relaxation through the relative motion of electron and nucleus. If we assume it is of the form $A_1 \vec{I} \cdot \vec{S}$, it induces transitions $(b') \longleftrightarrow (a)$. If this is the only term in the time-dependent part of Eq. (5.15) and if nuclear relaxation without accompanying electron spin flips has a very small probability, then it follows that $f^{(1)} = 1$, $f^{(2)} = 0$, $f^{(3)} = 0$, and

$$\frac{N_+}{N_-} = \frac{a + a'}{b + b'} = \frac{a}{b} \approx 1 + 2\Delta = 1 + \frac{|\gamma_e| \hbar H_0}{kT} \quad (5.18)$$

as in the Overhauser effect in metals. The term $\gamma_e \hbar \vec{H}' \cdot \vec{S}$ produces nuclear relaxation by random electron spin flips. This term induces strong electronic transitions $(a) \longleftrightarrow (a')$ and $(b) \longleftrightarrow (b')$, weak nuclear transitions $(a') \longleftrightarrow (b')$ and $(a) \longleftrightarrow (b)$ because of the small admixture in the eigenstates, and weak transitions $(b') \longleftrightarrow (a)$. If this is the only term in the time-dependent part of Eq. (5.15) and if the spectrum of H' is isotropic and white, then it follows that $f^{(1)} = f^{(3)}$, $f^{(2)} = 0$ and

$$\frac{N_+}{N_-} = \frac{a}{b} = 1 + \Delta = 1 + \frac{|\gamma_e| \hbar H_0}{2kT}, \quad (5.19)$$

which is just one-half the enhancement predicted in Eq. (5.18). It is clear from Fig. 6 that Eqs. (5.18) and (5.19) predict a positive nuclear magnetization when γ_n is positive and a negative nuclear magnetization when γ_n is negative. Abragam⁽¹⁰⁾ treats intermediate cases where random relative motion and random electron flips compete in producing nuclear relaxation in a paramagnetic ion, and he considers the situation where one of the resonances is saturated but not the other (say $a = a'$ but not $b = b'$).

However, he does not consider the intermediate case involved when one or both of the electron spin resonances is only partially saturated (i.e., $s < 1$). His arguments should be generalized to cover this situation for the following reason. Suppose an NMR experiment is performed, the frequency being $\omega_n = 2\delta kT$. In Fig. 6a the power absorbed by virtue of $a > b$ will be emitted by virtue of $a' > b'$ and there will be no net absorption of energy if $a = a'$, $b = b'$. It is reasonable to suppose that a maximum nuclear resonance absorption or emission effect can be produced here when $s = \frac{1}{2}$.

It is clear from the detailed discussion presented in Section 5 that a negative nuclear magnetization may be achieved by saturating the electron spin resonance if either of the following sets of conditions are satisfied:

$$\begin{array}{ll}
 (1) \quad \gamma_e < 0 & (1) \quad \gamma_e < 0 \\
 (2) \quad \gamma_n < 0 & \text{or} \quad (2) \quad \gamma_n > 0 \\
 (3) \quad \Delta m_S + \Delta m_I = 0 & (3) \quad \Delta m_S + \Delta m_I = \pm 2
 \end{array}$$

The first set of conditions is normally satisfied in a metal or a paramagnetic ion in a solid providing, of course, the nuclear magnetic moment is negative. The second set of conditions is normally satisfied in a liquid with paramagnetic impurities provided that the nuclear magnetic moment is positive.

In subsequent sections of this report we shall examine the various systems which have been investigated experimentally. This should turn up some ideas as to what new systems would be profitably studied by this particular double resonance technique.

SECTION 6

Metals

Successful conduction electron spin resonance experiments⁽¹⁴⁾ have been made in Li, Na, K, Cs, and Be with frequencies ranging between 300 and 9000 Mc/sec. Samples have been either metal particles small compared to the skin depth or flat plates thick compared to skin depth. The line widths have been found in some instances to be temperature independent (Li and Be) and in other instances to be temperature dependent (Na, K, Cs). The widths range from 0.1 gauss (Na at 4°K) to 20 gauss (K at 140°K). The g values are approximately the free electron values ($g = 2.0023$). Negative g shifts, $\Delta g = (g_{\text{exp}} - 2.0023)$, have been observed for all cases except Be⁹, which has a $\Delta g = +9 \pm 1 \times 10^{-4}$.

Successful nuclear magnetic resonance experiments have been made on at least 19 metals.⁽¹⁵⁾ The NMR frequency in metals exhibit a "Knight shift" as a result of the small local magnetic field at the nuclei due to the

spin paramagnetism of the conduction electrons. This has been shown to be primarily due to the contact part of the hyperfine interaction [Eq. (5.12)] and ranges from about 0.02% (Li^7) to 2.5% (Hg^{199}). No Knight shift has been observed in Be^9 . It is perhaps not so well known that the electron-nuclear dipole-dipole interaction [Eq. (5.11)] also makes a contribution to the Knight shift in noncubic crystals.⁽¹⁶⁾ The effect depends on the angle between the crystalline axes and the external magnetic field.

Successful Overhauser effect experiments⁽¹⁷⁾ have been reported on Li^7 and Na^{23} . Enhanced nuclear resonance absorption was observed at 50 kc/sec in fields of 30.3 and 40.2 gauss, respectively. The electron spin resonances were saturated with the corresponding applied frequencies at 84 and 124 Mc/sec. The temperature for the Li experiment was at about 70°C and it was considerably above room temperature for Na. The Li NMR signal was found to increase by a factor of about 110, which is considerably smaller than the optimum theoretical value of $|\gamma_e|/\gamma_n = 1690$. The enhancement was reduced by other nuclear relaxations which contributed to $f^{(3)}$ [see Eqs. (5.5) and (5.6)]. The Na NMR signal was found to increase by a factor of about 10, which is again much smaller than the theoretical limit. The reason for this was that the electron resonance line width was about 12 gauss under the conditions of observation and an H_1 of only 1 to 2 gauss was produced by the saturating oscillator over the sample volume. The saturation factor was therefore ~ 0.01 . Although these experiments were not carried out under optimum conditions of high H_0 and low T , they nevertheless constituted a striking confirmation of Overhauser's theoretical prediction. No low-temperature, high-field results have been reported on Li and Na as yet, nor have there been any experiments done on other metals.

The nuclear polarization achieved by Carver and Slichter was negligible for the values of H_0/T used and, consequently, no shift in the electron resonance frequency was observed. This shift is called the "Overhauser shift" and is the analogue of the Knight shift. It is very interesting that the algebraic sign and magnitude of the Overhauser shift can be used to determine the algebraic sign and magnitude of the nuclear polarization. Further, as the electron spin resonance is saturated, it is clear that both the isotropic and anisotropic Knight shift will vanish linearly with s . Consequently, both the shape and position of the EPR line and the NMR line are changed in an interesting fashion in an Overhauser effect experiment.

Beryllium presents some intriguing problems and possibilities, and merits further theoretical and experimental study. A successful Overhauser effect on beryllium would be most interesting. Be^9 has a nuclear spin $I = \frac{3}{2}$, a negative nuclear magnetic moment $\mu_n = -1.774$ nuclear magnetons, and a nuclear quadrupole moment⁽¹⁸⁾ of $Q = 0.029 \times 10^{-24} \text{ cm}^2$. One would expect a negative rather than a positive $\Delta g = +9 \times 10^{-4}$ as observed in EPR.⁽¹⁹⁾ The line width⁽¹⁹⁾ is rather large, ~ 13 gauss, which would make saturation of the electron spin resonance difficult. However, this width is temperature independent, which means it is probably due to impurities. This situation could

probably be improved by using small Be metal particles of high purity and doing the electron spin resonance at low temperatures where the line width should decrease. In view of its negative nuclear magnetic moment, Be should exhibit a negative nuclear magnetization when the electron spin resonance is saturated. This could be detected by the enhanced emission of a nuclear magnetic resonance signal and by a negative Overhauser shift. This will occur providing the $\vec{I} \cdot \vec{S}$ interaction is significant for nuclear relaxation. The absence of a Knight shift casts some doubt on this, but other evidence points to a substantial S state character in the metallic wave function. The measured Knight shift in Be⁹ is 0.000% which is quite surprising.⁽¹⁵⁾ The predicted value is 0.01%. One possible explanation is that the Knight shift is masked by a compensating negative shift produced by the second-order nuclear quadrupole interaction.⁽¹⁶⁾ This question too could be resolved if it is possible to saturate the electron spin resonance in Be, since the Knight shift would disappear but the negative nuclear quadrupole shift in the nuclear resonance would remain.

It would be very interesting to perform Overhauser effect experiments on other metals but they present several difficulties:

(1) In view of the high conductivity of metals, there is but a small depth of penetration in a microwave field. This difficulty can be met by using particles small compared to the skin depth. Particle dispersions have been prepared ultrasonically in paraffin wax or by precipitation in frozen metal-ammonia solutions. It is also possible in some cases to prepare colloidal particles of a diameter ~ 200 Å. Thick plates of metals have been used for EPR work. The resulting line shapes are asymmetrical and are accounted for quite well by Dyson's theory.⁽²⁰⁾ However, Carver and Slichter⁽¹⁷⁾ point out that the effects of saturation when the electrons diffuse in and out of the skin depth are not known.

(2) For a given level of saturation, metals exhibit a lower nuclear polarization than nonconducting paramagnetics. This is the case especially for small s and high H/T ratio, as pointed out in Section 5.

(3) The most serious difficulty is the short value of the electron spin lattice relaxation time. In metals $T_1 = T_2$ and a short T_2 means very broad lines, which are difficult to observe and extremely difficult to saturate. Elliott⁽²¹⁾ has developed a theory which considers the probability of an electron spin flip via spin-orbit coupling when there is a collision between a conduction electron and a phonon. The relaxation time is found to be

$$T_1 = \alpha T_R / (\Delta g)^2, \quad (6.1)$$

where $\alpha \approx 1/30$, T_R is the collision relaxation time which can be found from resistivity data, and Δg is the electron g shift which is a measure of the strength of the spin-orbit interaction. For Na at 300°K, $T_R = 3 \times 10^{-14}$ sec,

$\Delta g = -8 \pm 2 \times 10^{-4}$ and hence $T_1 \cong 2 \times 10^{-9}$ sec, which is in fair agreement with $T_1(\text{expt}) \cong 9 \times 10^{-9}$ sec. The important point to note is that Δg increases with increasing Z and hence T_1 becomes so short for the heavy metals that no EPR is observable. Thus for Li^7 : $\Delta g = \leq \pm 1 \times 10^{-4}$; Na : $\Delta g = (-8 \pm 2) \times 10^{-4}$; K : $\Delta g = (-70 \pm 50) \times 10^{-4}$; and for Cs : $\Delta g = (-700 \pm 200) \times 10^{-4}$. A satisfactory theory of the g shifts for the alkalis has been worked out by Brooks.⁽²²⁾ It is possible that this difficulty can be circumvented by using metal-ammonia solutions. Another possibility is to do a double resonance on neutral metal atoms present as impurities in one of the alkali halides. We shall discuss these topics in more detail in subsequent sections of this report.

A good deal of the material in Section 6 on metals has been obtained from an excellent survey: Microwave Properties of Solids by Baggeley and Owen.⁽²³⁾

SECTION 7

Metal-Ammonia Solutions

If an alkali metal like Na or K is dissolved in ammonia, the free atom will ionize in solution: $\text{Na} \rightleftharpoons \text{Na}^+ + e$. The positive metal ion has full, closed shells with no unpaired electrons. The electrons form a "free gas." Successful electron spin resonance experiments⁽²⁴⁾ have been made with such solutions. The remarkable feature of these experiments is that the line widths are extremely narrow being of the order of 0.05 gauss and smaller. A theory of metal-ammonia solutions has been worked out by Kaplan and Kittel.⁽²⁵⁾ According to this theory, the electrons are trapped in "cavities" in the solution and interact by the contact part of the hyperfine interaction with the protons of the NH_3 surrounding the cavity. The line widths are small due to the motional narrowing associated with the rotation and diffusion of the NH_3 molecules.

The advantage of such metal-ammonia solutions for the observation of the Overhauser effect is that the EPR may be easily saturated. One would expect from the theory a positive nuclear polarization of the protons, since $\gamma_e < 0$, $\gamma_n > 0$, and $\vec{I} \cdot \vec{S}$ coupling is dominant. An Overhauser effect experiment has been carried out by Carver and Slichter⁽¹⁷⁾ on this type of solution. They used Na in NH_3 , ranging in concentration from 0.01 to 0.9 N. The static field used was 11.7 gauss. A time-varying field with $H_1 = 0.09$ gauss produced saturation values greater than 88% in all cases. The proton NMR signal was enhanced, but only in fairly concentrated solutions did this approach the value $|\gamma_e|/\gamma_p \approx 660$. Evidently nuclear spin relaxation by some interaction other than $\vec{I} \cdot \vec{S}$ short circuited the expected effect at low concentrations.

There are three disadvantages to metal-ammonia solutions:

(1) The metal merely provides a source of "free electrons." It is not the metal nucleus which one would expect to be polarized but rather the protons in NH_3 with which the electrons have an appreciable S state hyperfine interaction.

(2) If one is looking for a high polarization by the Overhauser effect, rather than for a substantial enhancement of the NMR absorption, it is necessary to go to low temperature. The solutions become solid at these temperatures and the motional narrowing of the EPR lines would no longer be effective. Saturation of the wider lines to be expected at lower temperatures would require larger values of H_1 and hence more microwave power.

(3) Increasing the concentration of the metal in NH_3 is evidently necessary to achieve a maximum effect. However, such an increase broadens the electron spin line width, making saturation more difficult, and introduces the possibility of electron-proton dipolar coupling,⁽²⁵⁾ which reduces the enhancement.

SECTION 8

Liquids Containing Paramagnetic Impurities

Three experiments confirming the general features of Abragam's theory⁽⁶⁾ of the Overhauser effect in liquids containing paramagnetic impurities have been performed. In each case the nucleus polarized was the proton. The polarization was negative as the theory predicts for $\gamma_e < 0$, $\gamma_n > 0$, and dipolar coupling.

Bennett and Torrey⁽²⁶⁾ investigated a solution of Na and naphthalene in 1, 2 dimethoxyethane. The naphthalene in the solution is ionized by the addition of an electron forming an ionic free radical.⁽²⁷⁾ The electron spin resonance of this free radical was detected at 50 Mc/sec in a field of 17.8 gauss. The line width was 2.6 gauss. The proton resonance of the solvent ether was detected at 76.8 kc/sec. By increasing the 50-Mc/sec voltage from 0 to 400 volts across a coil within which was located the sample and the nuclear detection coil, values of s from 0 to 20% were obtained.⁽²⁸⁾ Let A represent the amplitude of the NMR signal and A_0 the value of A when $s = 0$. Then according to the theory⁽⁶⁾ we can write

$$\frac{A}{A_0} = 1 + E = 1 - \frac{1}{2} \frac{|\gamma_e|}{\gamma_n} s, \quad (8.1)$$

where the enhancement in this case is given by $E = -\frac{1}{2} (|\gamma_e|/\gamma_n) s$. Clearly E is not the same as the nuclear polarization, P , but it is related to it.

(Sometimes in the literature enhancement and polarization are used interchangeably. It is possible to obtain an appreciable enhancement at any temperature, but appreciable polarization can only be obtained at temperatures in the liquid He range.) It is clear that, for $s = 0$, the detection of the NMR is by absorption of power. As s increases, the nuclear polarization increases in the negative sense, corresponding to a larger number of nuclei in the upper energy states. Now NMR detection is by stimulated emission suggesting, as the authors point out, that the Overhauser effect could be used for a low-noise molecular amplifier. This is illustrated in Fig. 7. Bennett and Torrey observed a substantially complete effect for each degree of saturation, which is in good agreement with the assumption that the proton spins relax via dipolar coupling with the free electron.

Fig. 7

Abragam, Combrisson and Solomon⁽²⁹⁾ investigated a solution of disulfonate of potassium in water. The static magnetic field used was 3000 gauss. The electron resonance presented a structure of three lines of about 1-gauss width. One of these lines was partially saturated. The proton resonance signal was found to decrease, go through zero and become negative with a negative enhancement of about 10. In this experiment, unlike that of Bennett and Torrey, the proton spin relaxation is partly dipolar and partly without accompanying electron spin flips.

J. Krebs⁽³⁰⁾ has made a preliminary study at the Naval Research Laboratory of a 7% molar concentration of the DPPH free radical in benzene. The static magnetic field was about 3400 gauss with a corresponding ESR frequency of 10,000 Mc/sec, and a proton NMR frequency of 15.3 Mc/sec. The ESR line width was of the order of 12 gauss and only about 3% saturation had been achieved. The proton resonance was found to decrease and invert with a negative enhancement of about 5. The proton observed was the proton in benzene, not that in the free radical.

These experiments on liquids clearly confirm the predictions of the theory regarding an "inverted Overhauser effect." However, only extremely small nuclear polarizations can be obtained at room temperature. Liquids are clearly not appropriate systems for low-temperature work.

SECTION 9

Free Radicals

All free radicals have unpaired electrons associated with them. Electron paramagnetic resonance has been used extensively to detect and observe these structures. The line widths are usually quite small and hence signals of strong intensity are obtained from small amounts. This permits the detection of very small concentrations. A considerable amount of work has been done on the organic salt α , α -diphenyl β trinitrophenyl hydrazyl: $(C_6H_5)_2 N - NC_6H_2(NO_2)_3$. This DPPH radical has an electron g value of 2.0036 and a line width of 2.9 gauss in a solid.

Ingram⁽³¹⁾ gives an excellent summary of paramagnetic resonance in free radicals.

A successful Overhauser effect in the DPPH free radical was reported in an early experiment by Beljers, Van der Kint and Van Wieringen.⁽³²⁾ They used a static magnetic field of 3300 gauss, a microwave frequency of 9000 Mc/sec and an rf frequency of 14 Mc/sec. As the microwave power in their 70-watt klystron increased above 3 watts, they observed an increase in the proton resonance absorption. It is interesting to compare this result with the experiment of Krebs⁽³⁰⁾ on the same free radical dissolved in benzene. These two experiments indicate that the proton spin lattice relaxation in a solid is via the contact part of the hyperfine interaction, and in a liquid is via the dipolar part of the hyperfine interaction. Ingram points out that the free electron in DPPH is mainly attached to the nitrogen rather than to the hydrogen atom of the molecule and that a greater change could have been observed by the Dutch group if they had looked at the nitrogen rather than the proton resonance. The abundant isotope of nitrogen N^{14} has $I = 1$ and a nuclear moment of +0.405 nuclear magneton. One would expect a positive nuclear polarization in the case of N^{14} if this experiment were carried out.

SECTION 10

Semiconductors

Successful electron spin resonance experiments on donors in Si and Ge have been made. The work on Si is reviewed by Baggeley and Owen.⁽²³⁾ The work on Ge was published quite recently and makes an interesting

comparison between Si and Ge.⁽³³⁾ So far all attempts to observe spin resonance from acceptors in Si and Ge have not been successful.

The donor impurities in both Si and Ge have been P, As and Sb. The g shifts are all negative and are considerably larger in Ge than in Si. The line widths in Si are about 2-3 gauss and in Ge about 10-11 gauss at liquid He temperatures. The evidence indicates that the electrons move in large S-like orbits.

The Overhauser effect has been observed in phosphorus-doped silicon by Abragam *et al.*⁽³⁴⁾ The weak conductivity of the sample simplified considerably the problem of the penetration of the saturating field, particularly at high frequencies. As a result of the small number of conduction electrons, the nuclear spin-lattice relaxation times are much longer than in metals. This permitted the Saclay group to separate completely in space and time the two operations: (1) polarization of the nuclei by application of an intense electronic frequency, and (2) observation of this polarization at the nuclear resonance frequency. Si^{29} is the only isotope of silicon which has a nonzero spin and magnetic moment: $I = \frac{1}{2}$, $\mu_N = -0.555$ nuclear magneton, $|\gamma_e|/\gamma_N = -3300$. Si^{29} has a natural abundance of 4.68%.

The experiment of Abragam *et al.* was performed in a static field of $H_0 = 3300$ gauss, a microwave frequency of 9200 Mc/sec, and at a temperature of 77°K. The electron spin resonance line width was 4 gauss. A saturation $s \cong 3.8\%$ was estimated. The sample contained 5×10^6 atoms of P per cm^3 where the relaxation time of the Si^{29} spins was five minutes. The observed enhancement was negative and equal in absolute value to 100, about 20% smaller than the optimum expected: $E = s |\gamma_e|/\gamma_N = -(3.8) \times 10^{-2} \times 3300 \cong -120$.

It should be possible, although somewhat more difficult, to obtain a similar inverted Overhauser effect in Ge. The only isotope of germanium with a nonzero spin is Ge^{73} where $I = \frac{9}{2}$ and $\mu = -0.877$ nuclear magneton. The broader line widths in the electron spin resonance lines in Ge make saturation much more difficult. The Ge^{73} nucleus has a quadrupole moment $Q = -0.2 \times 10^{-24} \text{ cm}^2$ and the nuclear quadrupole interaction would probably provide a means of nuclear relaxation which would compete with the $\vec{I} \cdot \vec{S}$ interaction. The enhancement can be written as

$$E = \frac{|\gamma_e|}{\gamma_N} \left(s \frac{T_N^{(1)}}{T_N \text{ total}} \right) = -18,900 \left(s \frac{T_N^{(1)}}{T_N \text{ total}} \right) \quad (10.1)$$

Although the factor in parentheses in Eq. (10.1) will notably be smaller in Ge^{73} than in Si^{29} for the reasons given, this is compensated in part by the fact that $|\gamma_e|/\gamma_N$ is 5.7 times greater and that Ge^{73} has a natural abundance of 7.67%, which is somewhat greater than that of Si^{29} .

A Knight shift of 0.018% has been observed⁽³⁵⁾ in Si^{29} . This increase in the nuclear magnetic resonance frequency depends, of course, on the concentration of conduction electrons. A measurement of the quenching of this shift should provide an independent value of the saturation parameter in an Overhauser effect experiment.

It is rather intriguing to speculate about the spin resonance of acceptors in Si and Ge. The "unpaired electron" in this case is a "hole." Dr. B. Smaller of this Laboratory has suggested that the magnetic moment of a "hole" is positive. Usually spin resonance experiments are performed using a time-varying field which is linearly polarized and at right angles to the static field: $\vec{H} = H_0 \vec{k} + 2H_1 \cos \omega t \vec{i}$. The sample absorbs energy whether the magnetic moment is positive or negative. It is well known, of course, that the algebraic sign of the magnetic moment can be determined by using a circularly polarized magnetic field. An Overhauser effect experiment on holes in Ge and Si would be quite interesting. If Smaller's suggestion is correct and if the holes have S-like orbits as do the electrons in donors, then one should observe a positive nuclear polarization in Ge^{73} and Si^{29} because now there is $\vec{I} \cdot \vec{S}$ coupling between a positive γ_e and a negative γ_n . Possibly the "hole" spin resonance has not been observed in Si and Ge because of a strong spin-orbit interaction leading to a large positive Δg and a broad line width.

SECTION 11

Color Centers

Spin resonance has been observed in F, V_3 and U centers and in $\text{Ag}^+ \text{Ag}^0$ in KCl, but not in V_1 centers. A diagram of some of these centers in an alkali halide is given in Fig. 8. A $\square$ denotes a positive or negative ion vacancy; e denotes an electron and h denotes a hole. An F center is a negative ion vacancy and an unpaired electron. A V_3 center consists of two adjacent positive ion vacancies and a hole. A V_1 center is a positive ion vacancy and a hole. A U center is a negative ion vacancy occupied by an H^- ion.

Fig. 8

The g shift is negative for electrons and positive for holes. The line widths depend on concentration and on temperature. Many of the line widths reported are quite broad being ~ 50 gauss.

There are two systems which have been investigated at the Argonne National Laboratory⁽³⁶⁾ and which appear to hold some promise for an Overhauser effect experiment.

1. $\text{Ag}^\circ\text{Ag}^+$ in KCl. This is prepared by mixing AgCl with KCl in the melt and then growing single crystals which contain about 10^{18} Ag^+ ions/ cm^3 in the host. The crystal is irradiated with X rays or with γ rays from Co^{60} to produce $\text{Ag}^\circ\text{Ag}^+$. The silver ion, of course, has no unpaired electron. The Ag° has an unpaired electron as in the metal atom, which makes possible observation of the spin resonance. Both stable isotopes of silver, Ag^{107} and Ag^{109} , have spin values of $\frac{1}{2}$ and negative nuclear magnetic moments: $\mu_n^{107} = -0.113$ nuclear magneton, $\mu_n^{109} = -0.130$ nuclear magneton. The observed electron spin line widths are evidently narrow enough (~ 1 gauss) so that appreciable saturation of the ESR could be achieved. If the silver nuclear spin is coupled to the electron by the $\vec{I} \cdot \vec{S}$ interaction, which is the most plausible assumption, the saturation of the ESR should produce a negative nuclear magnetization which could be detected by the induced emission of an NMR signal. The expected enhancement would be

$$\left. \begin{aligned} E^{107} &= + \frac{|\gamma_e|}{\gamma_n^{107}} s \cong -16,200s \\ E^{109} &= + \frac{|\gamma_e|}{\gamma_n^{109}} s \cong -14,100s \end{aligned} \right\}, \quad (11.1)$$

where s is the saturation parameter. The essential difficulty involves the number of silver nuclei present and the unfavorable ratio of Ag° to Ag^+ . The Ag° concentration can probably be increased to $\sim 5 \times 10^{17}/\text{cm}^3$ by irradiating the sample for a longer time. Another possibility is to put in Ag atoms by additive coloring. Although this might produce a higher concentration of Ag atoms, once these atoms become aggregated in colloidal clusters the spin-lattice relaxation time might become extremely short making saturation of the resonance more difficult.

2. F_2^- in LiF. This system is of the same type as that studied by Kanzig⁽³⁷⁾ and by Smaller, Delbecq and Yuster.^(36,38) The unpaired holes are produced by X or γ irradiation. The g shifts are positive as expected for a hole. One would expect the magnetic moment of the hole to be positive, as in acceptors in Ge, according to Smaller's suggestion. This could be tested directly by using a circularly polarized, rather than a linearly polarized, time-varying magnetic field. If the hole resonance is saturated one should obtain a negative nuclear polarization of the fluorine nuclei. F^{19} has a spin of $\frac{1}{2}$, a magnetic moment $\mu_n = +2.13$ nuclear

magneton, and a natural abundance of 100%. The theoretical enhancement assuming $\vec{I} \cdot \vec{S}$ coupling of the F^{19} nuclei to the holes is

$$E = - \frac{|\gamma_e|}{\gamma_n} s = -780s \quad (11.2)$$

The nucleus has no quadrupole moment, having a spin $I = \frac{1}{2}$, and consequently nuclear relaxation via the quadrupole interaction would not compete with the $\vec{I} \cdot \vec{S}$ interaction. There might however be other contributions to $f^{(3)}$. (See Section 5). Similar experiments could be done with Cl_2^- in KCl or NaCl and Br_2^- in KBr. Values of I , μ_n in nuclear magnetons, γ_e/γ_n and Q in barns are given for the chlorine and bromine isotopes in Table 1. One unfavorable feature of this proposed experiment is the fact that the unpaired hole is probably shared primarily by the six nearest negative ions and that the nuclear resonance of the halide ions which do not "see" the hole might mask the polarization of those which do. This matter should be looked into further, with particular reference to the papers of Kanzig⁽³⁷⁾ and of Inui, Harasawara and Obata.⁽³⁹⁾

TABLE 1

	I	μ_n	γ_e/γ_n	Q	Natural Abundance
Cl^{35}	$\frac{3}{2}$	0.82	6700	-0.079	75.4%
Cl^{37}	$\frac{3}{2}$	0.68	8100	-0.062	24.6%
Br^{79}	$\frac{3}{2}$	2.11	2600	+0.26	50.52%
Br^{81}	$\frac{3}{2}$	2.27	2400	+0.21	49.48%

Conclusion

The results of this report can be summarized as follows. Paramagnetic resonance can be observed in any system which has an unpaired electron or hole. Appreciable saturation of this resonance can be achieved providing the line width is not too broad. Nuclei with nonzero magnetic moments which relax at least in part via their coupling with the electrons will become polarized. In general, one can expect the polarization to be larger the lower the temperature and the higher the static magnetic field. The signs of the polarization depend on whether the coupling is primarily $\vec{I} \cdot \vec{S}$ or dipolar and on the signs of γ_e and γ_n . In solids and in metal-ammonia solutions the electrons have a reasonably high probability of being in the immediate vicinity of the nucleus where the contact interaction is important. In liquids the electrons have a much less highly localized

position and one can expect dipolar coupling to be the important nuclear relaxation mechanism. In Table 2 the various possible combinations are listed. The examples encircled have not yet been observed. The other examples have been observed.

TABLE 2

γ_e	γ_n	Coupling	Nuclear Polarization	Example
-	+	$\vec{I} \cdot \vec{S}$	+	$\text{Li}^7, \text{Na}^{23}, \text{H}^1$
-	-	$\vec{I} \cdot \vec{S}$	-	$\text{Be}^9, \text{Si}^{29}, \text{Ag}^{107}, \text{Ag}^{109}$
-	+	Dipolar	-	H^1
-	-	Dipolar	+	
+	-	$\vec{I} \cdot \vec{S}$	+	$\text{Si}^{29}, \text{Ge}^{73}$
+	+	$\vec{I} \cdot \vec{S}$	-	$\text{F}^{19}, \text{Cl}^{35}, \text{Cl}^{37}, \text{Br}^{79}, \text{Br}^{81}$
+	-	Dipolar	+	
+	+	Dipolar	-	

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NOTE ADDED IN PROOF

There are two important points in this report which further discussion has clarified and corrected.

First, the gyromagnetic ratio of a "hole" in a solid should have the same algebraic sign as the gyromagnetic ratio of an electron. It is clear, of course, that the gyromagnetic ratio of a filled shell plus one is negative, since the only contribution to the magnetic moment comes from the extra unpaired electron. One is easily led to believe that the gyromagnetic ratio of a filled shell minus one is positive - a belief reinforced by analogy with the positron. However, a single electron in an S shell poses obvious difficulties. Kittel, in a private communication, has pointed out that the algebraic sign of the gyromagnetic ratio is independent of the condition of the shell.

$$\gamma \equiv \frac{\sum \mu_i}{\sum S_i} = \gamma_e \frac{\sum S_i}{\sum S_i} = \gamma_e$$

Second, the $\text{Ag}^0 \text{Ag}^+$ and F_2 in LiF systems are not as promising for Overhauser effect experiments as appeared at first sight. The reason for this is that the unpaired electron or hole gives rise to a rather large local magnetic field at the nucleus: $|A_0| \gg |\gamma_n| \hbar H_0$. The nuclear magnetic resonance frequency is thus $\omega_n = \mathcal{L}^0 kT = A_0/\hbar$ rather than $|\gamma_n| H_0$ and the expected enhancement would be $\sim s |\gamma_e| \hbar H_0 / A_0$ rather than $s |\gamma_e| / \gamma_n$ as given in Eqs. 11.1 and 11.2.

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$$s_{\text{Bennett and Torrey}} = s/(1-s).$$
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